

BARRIER STACK WITH IMPROVED BARRIER PROPERTIES**Field of the Invention**

The present invention relates to a barrier stack
5 used in, for example, integrated circuits (ICs) which
reduces diffusion of elements, such as oxygen. More
particularly, the barrier stack reduces oxidation of the
plug in capacitor over plug structures.

10 Background of the Invention

Memory ICs comprise a plurality of memory cells
interconnected by bitlines and wordlines. A memory cell
includes a transistor coupled to a capacitor for storage
of a bit of information. To realize high density memory
15 ICs, the memory cells employ a capacitor over plug
structure (COP), as shown in Fig. 1. The structure
includes a capacitor 140 having a dielectric layer 146
located between first and second electrodes 141 and 142.
The capacitor is coupled to a conductive plug 170.

20 Typically, a high temperature anneal in an oxygen
(O₂) ambient is required to improve the properties of the
dielectric layer, particularly for high K dielectric and
ferroelectric materials. During the anneal, O₂ diffuses
through the capacitor and oxidizes the plug. This can
25 lead to performance degradation and, in some cases,

failures as a result of increased plug resistivity or electrical open connections.

To prevent diffusion of oxygen through the capacitor, a barrier layer formed from iridium is 5 provided between the lower electrode and the plug. An adhesion layer is provided to promote adhesion between the barrier layer and interlevel dielectric layer 118, such as silicon dioxide (SiO_2) or silicon nitride (SiN). Iridium is used due to its good barrier properties 10 against O_2 . In conventional processing, the barrier layer and electrode have vertical grain boundaries 121 and 123 which connect at the interface 143, as shown in caption A. The connection of the vertical grain boundaries of the layers provides diffusion paths for O_2 . At high 15 temperatures (e.g., $> 600^\circ C$), O_2 can easily diffuse through the grain boundaries of the barrier layer to oxidize the adhesion layer and the plug.

From the foregoing discussion, it is desirable to provide an improved barrier layer for reducing oxidation 20 of the plug in a capacitor over plug structure.

Summary of the Invention

The invention relates to an improved barrier stack for inhibiting diffusion of atoms or molecules, such as 25 O_2 . Such barrier stack is particularly useful in, for

example, COP structures of memory cells. In one embodiment, the barrier stack is employed in a ferroelectric capacitor. The barrier stack can also be used in other types of capacitors, such as high k 5 dielectric capacitors.

In one embodiment, the barrier stack comprises at least first and second barrier layers in which the grain boundaries of the first and second barrier layers are mismatched. In one embodiment, the barrier layers are 10 conductive. The barrier layers are selected from a group of barrier materials comprising Ir, Ru, Rh, Pd, or alloys thereof. The first and second barrier layers need not be formed from the same material. By providing mismatched grain boundaries, the interface of the layers block the 15 diffusion path of oxygen.

In another embodiment, the grain boundaries of the first barrier layer are passivated with elements. In one embodiment, the grain boundaries are passivated with O₂. The O₂ stuff the grain boundaries of the barrier layers. 20 Alternatively, elements larger than the grain boundaries of the barrier layer are used to passivate the grain boundaries. Such elements block the grain boundaries of the barrier layer. The grain boundaries, for example, are passivated using a rapid thermal oxidation, which 25 also forms a thin oxide layer on the surface of the first

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barrier layer. Passivating the grain boundaries of the first barrier layer further enhances the barrier properties of the barrier stack. Alternatively, either all or some of the barrier layers are passivated with 5 elements, such as O₂.

The barrier stack, for example, is disposed between the plug and first or lower electrode of a capacitor structure. Optionally, an adhesion layer can be provided beneath the barrier layer.

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Brief Description of Drawings

Fig. 1 shows a cross-sectional view of a capacitor on plug structure;

Fig. 2 shows a ferroelectric memory cell;

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Fig. 3 shows one embodiment of the invention for reducing diffusion of oxygen; and

Figs. 4-6 show a process for fabricating a capacitor over plug in accordance with one embodiment of the invention; and

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Figs. 7-8 are TEMs of experiments conducted on a barrier stack formed in accordance with one embodiment of the invention.

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Detailed Description of the Invention

Fig. 2 shows a ferroelectric memory cell 201 with a transistor 230 and a capacitor 240. A second terminal 232 of the transistor is coupled to a first terminal 241 5 of the capacitor. Gate 233 and first terminal 231 of the transistor are respectively coupled to a wordline 250 and bitline 260. Coupled to a second terminal 242 of the capacitor is a plateline 270. The capacitor uses the hysteresis polarization characteristic of the 10 ferroelectric material for storing information. The logic value stored in the memory cell depends on the polarization of the capacitor. To change the polarization, a voltage which is greater than the switching voltage (coercive voltage) needs to be applied 15 across the capacitor's electrodes via the bitline and plateline. The polarization of the capacitor depends on the polarity of the voltage applied. An advantage of the ferroelectric capacitor is that it retains its polarization state after power is removed, resulting in a 20 non-volatile memory cell.

Referring to Fig. 3, a ferroelectric capacitor 340 employing a barrier stack 390 in accordance with one embodiment of the invention is shown. The capacitor includes a ferroelectric layer 346, such as lead 25 zirconium titanate (PZT). Strontium bismuth tantalum

(SBT) or other types of ferroelectric materials are also useful. The ferroelectric layer is located between first and second electrodes 341 and 342. The electrodes, for example, comprise a noble metal such as platinum. Other 5 types of conductive materials, for example, SrRuO_3 , $\text{La}_{0.5}\text{Sr}_{0.5}\text{O}_3$, LaNiO_3 , or $\text{YBa}_2\text{Cu}_3\text{O}_7$, are also useful. The upper and lower electrodes can be formed from the same or different materials.

A conductive plug is electrically coupled to the 10 lower electrode of the capacitor. The plug is formed from a conductive material such as polysilicon (poly-Si) or tungsten (W). Other conductive materials are also useful. The plug is, for example, coupled to a diffusion region of a transistor of the memory cell. The gate of 15 the transistor is coupled to a wordline and the other diffusion region is coupled to the bitline. The upper electrode is coupled to the plateline.

To prevent oxidation of the plug, a barrier stack 390 is located between the lower electrode and the plug. 20 An adhesion layer 349 is provided between the plug and barrier stack to promote adhesion of the barrier layer to the interlevel dielectric layer 118. The adhesion layer can be formed from, for example, titanium (Ti), tantalum (Ta), titanium nitride/titanium (TiN/Ti), tantalum 25 nitride/tantalum (TaN/Ta), tantalum nitride/titanium

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(TaN/Ti) or other adhesion promoting materials. In applications where the plug comprises polysilicon, a silicide pre-layer, such as titanium silicide (TiSi), is used to reduce or minimize contact resistance between the 5 plug and adhesion layer. The adhesion layer can also serve to reduce or minimize diffusion of silicon (Si) from the plug into the barrier layer.

In accordance with the invention, the barrier stack comprises at least first and second barrier layers 347 10 and 348. The barrier layers are, in one embodiment, conductive, creating a conductive barrier stack to electrically couple the lower electrode to the plug. The barrier layers, for example, comprise iridium (Ir). Other types of barrier material, such as ruthenium (Ru), 15 rhodium (Rh), palladium (Pd) or alloys thereof, are also useful. The different barrier layers of the stack can be formed from either the same or different materials. In one embodiment, the grain boundaries 323 and 321 of the barrier layers are mismatched (e.g., not aligned). By 20 mismatching the grain boundaries, the interface between the different barrier layers serve to block the diffusion path of O₂, thus improving the barrier properties of the barrier stack. The grain boundaries of the second barrier layer and upper electrode can also be mismatched

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to further improve barrier properties of the barrier stack.

In one embodiment, the grain boundaries at or near the surface of the first barrier layer are passivated (e.g., stuffed). In one embodiment, the grain boundaries are passivated with O₂. Other elements may also be used to passivate the grain boundaries. Various techniques, such as an anneal in an oxidizing ambient, can be used to passivate the grain boundaries. Oxidizing ambient includes, for example, O₂, ozone (O₃) or NO_x(0<x<2). Other techniques for passivating the grain boundaries, which include depositing a thin oxide layer over the barrier layer, are also useful. The thin oxide layer can be deposited by, for example, thermal oxidation. Other deposition techniques can also be used. By passivating the grain boundaries, the diffusion of O₂ is further inhibited.

In a preferred embodiment, the grain boundaries are passivated using a rapid thermal oxidation (RTO) process. The RTO also forms a thin oxide layer on the surface of the barrier layer. The thin oxide layer advantageously promotes mismatching of the grain boundaries between the first and second layer. In another preferred embodiment, the grain boundaries at or near the surface of the second

barrier layer are also passivated with O₂ to further improve the barrier properties of the barrier stack.

Additional barrier layers can be included in the barrier stack. The grain boundaries of adjacent barrier layers are mismatched. In one embodiment, at least the grain boundaries of the bottom barrier layer are passivated at or near its surface. Preferably, the grain boundaries of some or all the barrier layers are passivated at or near their surfaces. Using multiple barrier layers with mismatched boundaries improves the barrier properties of the stack, advantageously enabling the use of thinner barrier stack or layer without sacrificing reliability.

In another embodiment, elements larger than the
15 grain boundaries are used to passivate the grain
boundaries at or near the surface of a barrier layer.
Such elements block the grain boundaries, eliminating the
diffusion path to the plug.

Referring to Figs. 4-6, a process for fabricating
20 the barrier stack in accordance with one embodiment is
shown. The barrier stack is employed, for example, to
reduce or prevent oxidation of a plug in a capacitor over
plug structure of a memory cell. As shown, a substrate
401 is shown. The substrate comprises a semiconductor
25 substrate such as silicon. Other types of substrate,

such as silicon on insulator, can also be used. The substrate is prepared with an ILD 118 formed thereon. The ILD, for example, comprises SiO_2 . Other types of dielectric materials, such as silicon nitride (SiN), 5 titanium oxide (TiO_2), or aluminum oxide (Al_2O_3) are also useful. A plug 370, which is coupled to a diffusion region of a transistor 230, is formed in the ILD. The plug, for example, comprises tungsten or poly-Si. Other types of conductive materials are also useful. Various 10 known deposition and patterning techniques can be used to provide the prepared substrate.

Referring to Fig. 5, an adhesion layer 349 is deposited over the dielectric layer. The adhesion layer comprises, for example, titanium (Ti). Other types of 15 adhesion layers, such as tantalum (Ta) or titanium nitride/titanium (TiN/Ti), tantalum nitride/tantalum (TaN/Ta), tantalum nitride/titanium (TaN/Ti), or other adhesion promoting materials can also be used. The adhesion layer is deposited by conventional techniques. 20 Such techniques include, for example, DC sputtering or chemical vapor deposition (CVD). If the plug comprises poly-Si, a pre-layer comprising silicide is formed on the ILD prior to the adhesion layer. The silicide layer can be formed by, for example, annealing of sputtered metal 25 on poly-Si.

The process continues to form the layers of the barrier stack 390. In one embodiment, a first barrier layer 347 of the barrier stack is deposited on the adhesion layer. The first barrier layer comprises, for example, Ir. Other types of barrier layer, such as Ru, Rh, Pd or alloys thereof, are also useful. Various known techniques, including chemical vapor deposition (CVD), chemical solution deposition (CSD), electro-plating, hydro-thermal synthesis or physical vapor deposition (PVD) can be used to form the barrier layer.

In accordance with one embodiment of the invention, the first barrier layer is annealed in an O₂ ambient. During the anneal, O₂ from the ambient fills the grain boundaries of the barrier layer near its surface. In one embodiment, the anneal also oxidizes the barrier layer, forming a thin oxide layer 563 on the surface thereof. The oxide comprises oxide of the material used to form the barrier layer. For example, an IrO_x is formed if an Ir barrier layer is used. Additionally, the anneal relieves the stress between the adhesion layer and barrier layer. Preferably, the anneal comprises an RTO. The RTO, for example, is performed at a temperature of 400-700°C for about 5-600 sec.

A second barrier layer 348 is deposited over the first barrier layer. The second barrier layer comprises,

for example, Ir. Other types of barrier layers are also useful. It is not necessary that the different barrier layers of the barrier stack are formed from the same material.

5 Due to the fact that the second barrier layer is formed over thin oxide layer and not the first barrier layer, the crystallization and grain growth behavior of the barrier layers are different. Specifically, the columnar grain growth of the second barrier layer is not
10 grown along the first layer's grain boundary, leading to a misfit grain growth between the barrier layers.

In an alternative embodiment, mismatch in grain growth can be facilitated by depositing a thin conductive layer over the first barrier layer which is different
15 from the first barrier layer. The conductive layer, for example, comprises a conductive oxide. Alternatively, using different first and second barrier layers are also useful. In yet another embodiment, different process parameters can be used to deposit the first and second
20 barrier layers to promote different grain growth (e.g., different grain sizes).

In another embodiment, after the second barrier is formed, an anneal in an oxidizing ambient is performed. Preferably, the anneal comprises an RTO in an oxidizing
25 ambient. The anneal forms an oxide layer over the second

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barrier layer as well as stuffing the grain boundaries near the surface of the second barrier layer.

Referring to Fig. 6, the process continues to form the capacitor on the barrier stack over the plug. In one embodiment, the process continues to form a ferroelectric capacitor. Forming other types of capacitors are also useful. The process includes sequentially forming first conductive electrode layer 341, ferroelectric layer 346, and second electrode layer 342. The electrode, for example, comprises a noble metal. Other types of conductive materials can also be used. In one embodiment, the ferroelectric material comprises PZT. Other types of ferroelectric materials, such as SBT, are also useful. Various known techniques can be used to form the different layers of the capacitor. Such techniques, for example, include CVD, chemical solution deposition (CSD), electroplating, hydro-thermal synthesis, or physical vapor deposition (PVD).

The various layers on the ILD are patterned to form the capacitor over plug structure. The layers are patterned using, for example, conventional mask and etch techniques. Other patterning techniques can also be used. After forming the capacitor, the substrate is annealed in an oxygen ambient to recover the electrical characteristics of the capacitor. The anneal for

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example, is performed at a temperature of about 500-800°C for about 1 minute to 5 hours. During the anneal, oxygen diffuses through the layer of the capacitor as well as the grain boundaries of the second barrier layer.

5 However, the diffusion path at the interface of the barrier layers are blocked due to the mismatch in grain boundaries of the barrier layers and stuffing of the grain boundaries of the first barrier layer near its surface with oxygen. Since diffusion of oxygen through 10 the bulk of the barrier layer is much slower than that along the grain boundaries, oxygen diffusing through the barrier stack is reduced. This reduces oxidation of the plug, thus improving reliability.

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Experiments

Fig. 7 shows TEM of a COP test structure 701 which includes a barrier stack 390 formed in accordance with one embodiment of the invention. The test structure includes a tungsten plug 770 formed in a SiO_2 ILD layer 738. A 10 nm thick titanium layer 794 is sputtered deposited over the plug. The titanium layer serves as an adhesion layer, promoting adhesion between the ILD and the subsequently formed barrier layer. The barrier includes first and second 70 nm thick iridium layers 747 and 749, each deposited by sputtering in 50 sccm of argon 25

gas for about 45 seconds. An RTO in O₂ is performed after the formation of the first and second iridium layers, each at 600°C for about 30 seconds to passivate the grain boundaries of the first iridium layer.

5 A 10 nm platinum electrode 741, a 10 nm strontium ruthineum oxide (SRO) 783, first 746a and second 70 nm PZT, 10 nm SRO, and 10 nm platinum electrode layers are sequentially sputtered over the barrier layer. An RTO was performed after the deposition of each SRO and PZT
10 layer. The RTO after formation of an SRO layer was performed in O₂ at 650°C for 30 seconds to crystallize the SRO layer while the RTO after deposition of a PZT layer was performed in O₂ at 650°C for 30 seconds. Due to the various RTOs, an iridium oxide layer 788 is formed
15 between the barrier layer and electrode 741. The layers above the first PZT layers were removed by the preparation process to acquire the TEM. As shown in Fig.
20 7, the interface between the plug and barrier layer has not been oxidized, evidenced by the relatively clean interface line 796 between the barrier and plug.

Fig. 8 shows a TEM of the structure of Fig. 7 after annealing in O₂ at 650°C for 2 hours. The post anneal serves to improve the properties of the ferroelectric layer. As shown in Fig. 8, the interface 796 between the
25 plug and barrier layer remains relatively unchanged after

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the anneal. This indicates that the barrier layer adequately prevented the diffusion of O₂ to the plug during the post anneal, thus avoiding oxidizing the plug.

While the invention has been particularly shown and described with reference to various embodiments, it will be recognized by those skilled in the art that modifications and changes may be made to the present invention without departing from the spirit and scope thereof. The scope of the invention should therefore be determined not with reference to the above description but with reference to the appended claims along with their full scope of equivalents.

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